EXHIBIT
A

A TEXT-BOOK OF

PRACTICAL ORGANIC CHEMISTRY

INCLUDING

QUALITATIVE ORGANIC ANALYSIS

By

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With diagrams and 8 photographs

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(ii) The crude selenium dioxide is placed in a large porcelain or silica crucible, which is supported in a hole made in a stout asbestos board. Two nested funnels are inverted over the crucible, the larger funnel having a plug of glass wool in the neck. The crucible is heated with a small flame until sublimation is complete (about 25 minutes). When the crucible has cooled, the resublimed selenium dioxide (*in long needle-like* crystals) is removed and stored in a tightly stoppered bottle. The yield is about 63 g.

Note.

Extreme care should be taken when working with selenium dioxide because of its poisonous properties.

17. **Silver nitrite.** Warm concentrated solutions of silver nitrate (containing 48 g. of $AgNO_3$) and potassium nitrite (containing 30 g. of KNO_2) are mixed, and the mixture is allowed to cool. The silver nitrite which separates is filtered off and washed with water. It may be recrystallised from water at 70°, and is dried either in a vacuum desiccator or in an air oven at about 40°; the yield is about 90 per cent. Silver nitrite should be stored in an tightly-stoppered amber bottle.

18. **Zinc cyanide.** Solutions of the reactants are prepared by dissolving 100 g. of technical sodium cyanide (97–98 per cent. NaCN) in 125 ml. of water and 150 g. of anhydrous zinc chloride in the minimum volume of 50 per cent. alcohol (1). The sodium cyanide solution is added rapidly, with agitation, to the zinc chloride solution. The precipitated zinc cyanide is filtered off at the pump, drained well, washed with alcohol and then with ether. It is dried in a desiccator or in an air bath at 50°, and preserved in a tightly stoppered bottle. The yield is almost quantitative and the zinc cyanide has a purity of 95–98 per cent. (2). It has been stated that highly purified zinc cyanide does not react in the Adams' modification of the Gattermann reaction (compare Section IV,121). The product, prepared by the above method is, however, highly satisfactory. Commercial zinc cyanide may also be used.

Notes.

(1) The only important precaution in this preparation is to ensure an excess of zinc chloride over sodium cyanide. If the latter is in excess, the zinc cyanide generally precipitates as a sticky mass, which is difficult to filter and unsatisfactory for the preparation of hydroxy-aldehydes.

(2) The cyanide content may be determined by titration with standard silver nitrate solution.*

II,51. CALCULATION OF YIELDS

The **theoretical yield** in an organic reaction is the amount which would be obtained under ideal conditions if the reaction had proceeded to completion, *i.e.*, if the starting materials were entirely converted into the desired product and there was no loss in isolation and purification. The **yield** (sometimes called the **actual yield**) is the amount of pure product which is actually isolated in the experiment. The **percentage yield** is

* For a convenient method, see Vogel, *Text Book of Quantitative Inorganic Analysis: Theory and Practice*, Second Edition, 1951, p. 263 (Longmans, Green and Co. Ltd.).

computed from the ratio between the weight of the pure product obtained and the weight calculated, *i.e.*,

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

In the calculation of yields, the term mol is usually employed. A mol (or mole or gram molecule) is equal to the molecular weight in grams. Hence the number of mols is equal to the weight of the substance in grams divided by the molecular weight.

Let us suppose it is desired to calculate the theoretical yield of ethyl maleate when 33 g. of silver maleate, suspended in dry ether, are treated with the calculated quantity of ethyl iodide (31·2 g.).

$$\begin{array}{l} \text{CHCOOAg} \\ \| \\ \text{CHCOOAg} \end{array} + 2C_2H_5I = \begin{array}{l} \text{CHCOOC}_2\text{H}_5 \\ \| \\ \text{CHCOOC}_2\text{H}_5 \end{array} + 2AgI$$

1 mol	2 mols	1 mol	2 mols
330 g.	312 g.	172 g.	470 g.

From the equation representing the chemical reaction involved, it is evident that 330 g. of silver maleate will theoretically react with 312 g. of ethyl iodide in ethereal solution to produce 172 g. of ethyl maleate. It follows, therefore, that 33 g. (0·1 mol) of silver maleate will react with 31·2 g. (0·2 mol) of ethyl iodide to give a theoretical yield of 17·2 g. (0·1 mol) of ethyl maleate. In practice, the actual yield found for these quantities is of the order of 16·0 g.; the percentage yield is therefore $(16{\cdot}0/17{\cdot}2) \times 100 = 93$ per cent.

After a little experience in the organic chemistry laboratory, the student will soon find that the yields frequently do not approach the theoretical values. This may be due to one or more of the following causes :—

(i) The reaction may not proceed to completion because the reverse reaction may occur under the given conditions and a state of equilibrium is established.

(ii) A portion of some of the reactants may be consumed in some alternative reaction (" side reaction "), which leads to products other than those desired; or, one or some of the components may be lost, *e.g.*, by volatilisation (because of its low boiling point or it may be carried away by gases evolved in the reaction) in spite of most careful manipulation.

(iii) Some of the desired product may be lost by further chemical change before it can be isolated.

(iv) Mechanical losses incident upon separating and purifying the product.

(v) The purity of some of the reagents may be uncertain, *e.g.*, they may contain varying amounts of water in their commercial forms.

In order to obtain an improved yield of the desired product, an excess over the proportion required by the chemical equation of one (or more) of the reactants is often used. In a given preparation, the selection of the reagent to be employed in excess will depend upon a number of factors; these include its relative cost and ease of removal after the reaction, and

its influence upon reducing the extent of "side reactions." Some examples follow, and these will incidentally illustrate the method of calculation of the percentage yield in such cases.

Two reactants. In the preparation of *n*-hexane, 61·5 g. of *n*-propyl bromide were treated with 23 g. of sodium and 18·0 g. of *n*-hexane were ultimately isolated.

$2C_3H_7{}^{\alpha}Br$	+	$2Na$	$\longrightarrow$	C_6H_{14}	+	$2NaBr$	
2 gram mols		2 gram atoms		1 gram mol			
246 g.		46 g.	yield	86 g.			(*Theory*)
61·5 g.		23 g.	yielded	18 g.			(*Practice*)

It is evident from the equation that the sodium is used in excess. Actually 61·5 g. of *n*-propyl bromide is 0·5 gram mol; this will react with 0·5 gram atom or 11·5 g. of sodium, so that 100 per cent. excess was actually employed. The theoretical yield of *n*-hexane will be 0·25 gram mol or 21·5 g., since 2 mols of *n*-propyl bromide give 1 mol of *n*-hexane. The actual yield was 18 g., hence the percentage yield is $(18/21{\cdot}5) \times 100 = 84$ per cent.

n-Butyl acetate was prepared by refluxing a mixture of 37 g. of *n*-butyl alcohol, 90 g. of glacial acetic acid and 2 g. of concentrated sulphuric acid, pouring into excess of water, washing the upper layer with saturated sodium bicarbonate solution, drying and distilling; the yield of ester was 54 g. Here the sulphuric acid acts as a catalyst and therefore does not appear in the equation.

$C_4H_9{}^{\alpha}OH$	+	CH_3COOH	$\longrightarrow$	$CH_3COOC_4H_9{}^{\alpha}$	+	H_2O	
1 mol		1 mol		1 mol		1 mol	
74 g.		60 g.		116 g.		18 g.	(*Theory*)
37 g.		90 g.		54 g.			(*Practice*)

The reactants are in the proportion of $37/74 = 0{\cdot}5$ mol to $90/60 = 1{\cdot}5$ mol, and it is therefore clear that the acetic acid is present in 200 per cent. excess. The theoretical yield must therefore be computed on the basis of the weight of *n*-butyl alcohol employed, and will be 0·5 mol or 58 g. The percentage yield is accordingly $(54/58) \times 100 = 93$ per cent.

Three reactants. Ethyl iodide may be prepared by the interaction between iodine, ethyl alcohol and red phosphorus. The quantities employed and the yield obtained in a particular experiment are given below the equation.

P	+	$5C_2H_5OH$	+	$5I$	$\longrightarrow$	$5C_2H_5I$	+	H_3PO_4	+	H_2O	
1 gram atom		5 gram mols		5 gram atoms		5 gram mols					
31 g.		230 g.		635 g.		780 g.					(*Theory*)
4·14 g.		27·5 g.		63·5 g.		73 g.					(*Practice*)
0·133 g. atoms		0·598 g. mols		0·500 g. atoms							(*Practice*)

To decide which component should be employed for the calculation of the yield of ethyl iodide, the weights of the reactants are first divided by the appropriate atomic or molecular weight in order to obtain the number of gram atoms or gram mols actually used. The equation shows that the alcohol and iodine react in the ratio of 5 : 5 or 1 : 1. Inspection of the results clearly shows that the alcohol is present in about 20 per

cent. excess, and on this basis 33 per cent. excess of phosphorus is employed. The yield is accordingly calculated from the weight of iodine (which, incidentally, is the most expensive component). The theoretical yield from 0·500 gram atom of iodine is 0·500 gram mol of ethyl iodide (since 5 gram atoms of iodine give 5 gram mols of ethyl iodide) or 78 g. The percentage yield is (73/78) × 100 = 94 per cent.

II,52. GENERAL INSTRUCTIONS FOR WORK IN THE LABORATORY

Before commencing any preparation in the laboratory, the student must carefully study the complete details of the experiment as well as the underlying theory. Not only should he have a clear idea of what is to be done and how he proposes to do it, but at all times he should be ready to give an intelligent reply to questions as to what he is doing and why he is doing it. The exercise may then be said to be truly scientific and not of the cookery book-recipe type. The student will soon realise that quite a number of experiments require somewhat prolonged periods of heating, refluxing or standing during which the whole of his attention is not required. A keen worker will make use of this time, *e.g.*, in writing up reports, planning other experiments, and cleaning and drying apparatus.

The results of all experiments must be recorded in a stiff-covered note-book (a loose-leaf note-book is not admissible) at the time the observations are made. If the experiment calls for records of weights, volumes, or other numerical results, these must be entered directly into the note-book and not on scraps of paper; the latter are liable to be lost and their use tends to develop untidy and slack habits on the part of the student. When the experiment is complete, the student should calculate the yield and then submit the laboratory note-book and the product, suitably labelled (including the melting or boiling point range and the weight), to the demonstrator or instructor. It is a good plan to submit at the same time a short summary of the results (name of preparation, yield, m.p. or b.p. range, etc.) on a sheet of paper to the demonstrator; the sheet will be retained for record purposes. If the work is approved, the student is permitted to proceed with the next experiment in the course.

Students are generally permitted to retain small specimens of their preparations: the main bulk, unless it is required for a succeeding preparation, must be returned to the chemical store. Solids may be kept in small specimen tubes and appropriately labelled (name of compound, m.p., details concerning method of purification, and date); if the compound exhibits signs of being deliquescent or hygroscopic, or otherwise affected by contact with air, the cork should be "waxed over" by painting it completely with molten paraffin wax. Liquids may be sealed off in specially prepared tubes. A short length of moderately thick-walled glass tubing is cleaned by immersion in a narrow cylinder containing "chromic acid cleaning mixture" (compare Section **II,2**), thoroughly washed with distilled water, followed by a little acetone, and is then dried by passing a current of warm air through it. One end is then sealed off in the blowpipe flame as in Fig. *II*, *52*, 1, *a*; students